



## Performance of Carbon Based Dye-Sensitized Solar Cells by Inclusion of Modified Low Cost Carbon Nanotubes

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### Abstract

Power production with zero green house gas emission is economically and environmentally desirable. Direct photovoltaic conversion of sunlight into electricity is therefore a highly attractive to unsustainable energy sources such as fossil fuels. The development of dye-sensitized solar cells, which have derived inspiration from photosynthesis, has opened up exciting new possibilities and paradigms for producing solar photovoltaic possibly at lower cost. The DSSCs can be considered to be electrochemical devices consisting of a photoanode, counter electrode, electrolyte & dye.

**Keywords:** Dye Sensitized Solar Cell; Carbon nanotube; Efficiency.

### 1. INTRODUCTION

Developing an inexpensive, renewable energy source is one of the most important scientific and technological challenges of our time. Solar energy is an inexhaustible energy source that could be harnessed to meet growing energy needs in near future. Solar energy can be harvested directly from sunlight using photovoltaic energy is close to an ideal way to utilize the nature's renewable energy flow. Silicon based solar cells primarily are utilized with solar panel, which makes these solar cells brittle, heavier, and bulky in their utilization. A solar cell made entirely from carbon, one of the most abundant elements on earth opens the door to much cheaper energy generation capabilities in the future. First-generation photovoltaic cells are the dominant technology in the commercial production of solar cells. Second generation of photovoltaic materials is based on the use of thin epitaxial deposits of semiconductors on lattice-matched wafers. Third generation photovoltaics are proposed to be very different from the previous semiconductor devices as they do not rely on a traditional p-n junction to separate photogenerated charge carriers. These new devices include photoelectrochemical cells, dye

sensitized solar cells organic or polymeric solar cells. Dye sensitized solar cells (DSSCs) are a relatively new class of thin film solar cells with promising high conversion efficiency at a low cost. Since 1991, following the demonstration of dye- sensitized solar cells for the first time by Prof. Michael Gratzel at EPFL, DSSCs have been attracting attention of both researchers and industries worldwide (Regan *et al.* 1991; Gratzel, 2001). These solar cells utilize two main components a photo anode consisting of light-absorbing dye molecules adsorbed on a semiconductor material, and an electrically conductive counter electrode that catalyzes an electrolyte redox reaction to regenerate electrons for the dye molecules. All carbon cells could be inexpensive, printable, flexible and tough enough to withstand extreme environments such as at high temperature or at high physical stress. Development of material engineering in the nanometer scale has generated new photovoltaic materials and systems that could potentially lead to realization of low-cost solar cells in the future. Carbon nanotubes have extraordinary electrical conductivity and light-absorption properties. In a typical thin film solar cell, the electrodes are made of conductive metals and Indium tin oxide. Materials like indium are scarce and becoming more expensive as the demand of solar

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cells. Carbon based transparent electrodes as the replacement of conventional FTO/ITO have been widely used in several solid-state optoelectronic devices such as organic thin film transistors, organic light emitting diodes, organic solar cells and solid state DSSCs. Currently platinum is a dominant catalyst counter electrode in DSSCs because of the high electrochemical activity (Yang *et al.* 2011; Zhang *et al.* 2012; Kim *et al.* 2006). While offering excellent electrical conductivity, catalytic activity, and corrosion resistance, Pt is also an expensive and relatively rare element. To lower materials cost and achieve feasible large-scale production, an alternative counter electrode material with excellent high conductivity as well as superior electrocatalytic activity is highly desirable. Because of the low cost, high durability, excellent catalytic activity, and electrical conductivity, carbon-based materials have been utilized as effective alternative counter electrode for many years. (Huang *et al.* 2012). Therefore, it came to our attention that the dramatically reduced cost and high stability of DSSCs could be achieved if FTO/ITO and Pt in DSSCs are replaced with carbon based materials at both working and counter electrode. In addition, carbon based electrodes have other advantages such as the abundance of material source, potentially scalable fabrication from the solution process, non-brittleness, chemical stability and optical transparency in the near infra red region. An electrolyte is a chemical system that provides an electrolytic contact between the solar cell electrodes. Carbon nanotubes based polymer electrolyte possess several advantages such as nanotubes channelize the flow of electrons in turn ordering the segmental motion along the polymer electrons hop through nanotubes-in polymer nanotube system, hope for ballistic transport in nanotubes and induce ordering in polymer. Researchers have had a hard time making carbon nanomaterials that collect electrons. It can be solved by picking the right flavor of nanotubes and giving them a chemical treatment called doping. Carbon nanotubes could be used in order to improve the efficiency of organic/ organic-inorganic hetero junction solar cells or as electrodes for solar cells. They could create novel all carbon based materials with new optoelectronic properties with highest power conversion efficiency.

## 2. WORKING PRINCIPLES OF DSSC

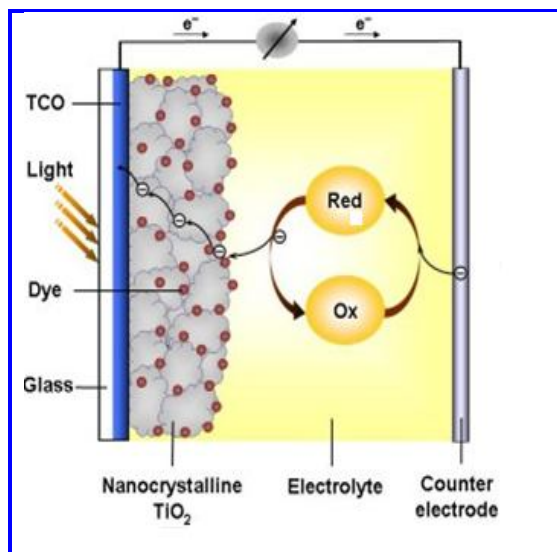
Dye sensitized solar cell is composed of nanocrystalline semiconductor oxide film electrode, dye sensitizers, electrolytes, counter electrode and transparent conducting substrate. Typically DSSC consists of a photoanode, which is made up of a wide band gap semiconductor like  $\text{TiO}_2$ ,  $\text{SnO}_2$ ,  $\text{ZnO}$  etc

with a monolayer of dye molecule adsorbed on it, an electrolyte tri-iodide and iodide redox couple and a conductive substrate coated with a catalyst (Pt, Carbon, etc) as cathode (Ramar *et al.* 2012; Chang *et al.* 2009). The choice of dye is also an important parameter. The first organic dye photosensitization was reported in 1887 (Nazeeruddin *et al.* 1993). In traditional DSSC, the standard dye was tris (2, 2'-bipyridyl-4, 4'- carboxylate ) ruthenium (II) ( $\text{N}_3$ ) dye. The function of carboxylate group in the dye is to attach the semiconductor oxide substrate by chemisorptions. The photovoltaic performance of  $\text{N}_3$  dye has been irreplaceable by other dye complexes since 1993. The operating mechanism of the solar cells is shown in Figure 1. Under the irradiation of sunlight, the dye molecular became photo-excited and ultra fastly injected an electron into the conduction band of the semiconductor electrode, then the original state of the dye is subsequently restored by electron donation from the electrolyte, usually the solution of an organic solvent or ionic liquid solvent containing the  $\text{I}_3^-/\text{I}^-$  redox system (Cherepy *et al.* 1997). The regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye. The iodide is regenerated, in turn, by reduction of tri-iodide at the counter electrode, the circuit being completed through the external load. The voltage generated under illumination corresponds to the difference between the Fermi level of the electron in the semiconductor electrode and the redox potential of the electrolyte. Over all, electric power is generated without permanent chemical transformation. Along with these processes, electrons in the conduction band of semiconductor may be recombined with the oxidized dye sensitizers or electron acceptor species in the electrolyte solution (Tachibana *et al.* 1996). Compared to FTO glass or metallic substrate materials CNTs have high electrochemical activity with interactive surface area. The high aspect ratios and large surface area of CNTs could be beneficial to exciton dissociation and charge carrier transport thus improving the power conversion efficiency (Wei *et al.* 2007). Recently platinized carbon nanotubes have proved to be more efficient in DSSCs as counter electrodes. (Hou *et al.* 2011; Nazeeruddin *et al.* 2011; Zhang *et al.* 2012) Cai *et al.* (2012), proposed an approach using Carbon nanotubes as both working electrodes and counter electrodes.

## 3. DSSC COMPONENTS

DSSC converts visible light into electricity based on the sensitization of wide bandgap semiconductors and is primarily comprised of photoelectrode, redox electrolyte and counter electrode. Other materials include transparent

conducting oxide and sealing agents. DSSC components have gone under various developments over the years in order to enhance the efficiency of the cell.



**Fig. 1: Schematic Diagram of Dye Sensitized Solar Cell**

### 3.1 Photosensitizers

One of the key elements in dye sensitized solar cells is photosensitizer. An efficient photosensitizer must fulfill certain requirements such as

- An intense absorption in the visible region.
- Strong adsorption onto the semiconductor surface.
- Efficient electron injection into the conduction band of the semiconductor.
- It should possess several =O or —OH groups capable of chelating to the Ti(IV) sites on the TiO<sub>2</sub> surface.

The most successful photo-induced electron transfer sensitizers employed so far in dye sensitized solar cells are ruthenium (II) polypyridyl complexes. The ruthenium complexes in DSSCs have exhibited power conversion efficiencies up to 12 % (Yella *et al.* 2011). Due to the high cost of ruthenium complexes and the scarce availability of those noble metals, looking for cheaper, simpler, and safer sensitizers becomes a challenging scientific problem (Campbell *et al.* 2007). Natural pigments, including chlorophyll, anthocyanin, nasunin, and carotenoids, can fulfill those requirements, and sensitization of TiO<sub>2</sub> by natural pigments has been reported (Wongcharee *et al.* 2008). Experimentally, natural

dye-sensitized TiO<sub>2</sub> solar cells have reached an efficiency of 7.1 % (Calogero *et al.* 2008). Whereas, Liu *et al.* have reported higher efficiency by mixing xanthophylls and chlorophyll natural pigments obtained from different plants (Liu *et al.* 2008). This indicates that the mixed pigments show synergistic effect in the energy transfer of the mesoporous TiO<sub>2</sub> solar cells. Sandqist *et al.* (2011) extracted betanin pigments from beet root using improved separation techniques and obtained efficiency as high as 2.7 %. This is the highest efficiency recorded for a dye sensitized solar cell containing a single unmodified natural dye sensitizer. Therefore, natural dyes open up a perspective of commercial feasibility for inexpensive and environmentally friendly dye sensitized solar cells.

### 3.2 Photo Electrode

Compared with various wide band gap semiconductors such as ZnO, SnO<sub>2</sub> and CdS, titanium dioxide is one of the most attractive photovoltaic material due to its interesting properties. Photoelectrodes made of materials such as silicon and cadmium sulfide decompose under irradiance in solution owing to photocorrosion. In contrast, oxide semiconductor materials, especially TiO<sub>2</sub> have good chemical stability under extreme operating conditions. It has strong oxidizing power, is non-toxic and exhibits long term photo stability.

The high dielectric constant of TiO<sub>2</sub> provides good electrostatic shielding of the injected electron from the oxidized dye molecule attached to the TiO<sub>2</sub>, thus preventing their recombination before reduction of the dye by the redox electrolyte. High refractive index of TiO<sub>2</sub> results in efficient diffuse scattering of the light inside the porous photoelectrode, which significantly enhances the light absorption (Anderson *et al.* 1979; Hamnett *et al.* 1979). Miyasaka *et al.* obtained high conversion efficiency up to 4.1% with an electrophoretic deposited TiO<sub>2</sub> layer following a chemical treatment and a thermal treatment of 150 °C for interconnecting TiO<sub>2</sub> particles (Miyasaka *et al.* 2004). Gratzel group developed the high efficiency (7.2 %) flexible solar cells based on a Ti- metal foil substrate for photoanode and a Pt-electrodeposited counter electrode on ITO-PEN, which is the highest efficiency for flexible DSSC (Ito *et al.* 2006). To prepare the semiconductor film electrode with uniform-size high-surface area, and the porous structure whose direction is perpendicular to the conducting substrate is one of the focuses of present research. Kongkanand *et al.* (2007), reported that the carbon nanotubes incorporated with TiO<sub>2</sub> structures could play an important role in

transporting the photogenerated electrons toward the conductive support.

### 3.3 Electrolyte

In dye sensitized solar cell, apart from being an electrically conducting medium, the electrolyte also regenerates the dye. In general, following are the criteria for materials to serve as electrolytes in DSSCs (Yu *et al.* 2011; Wu *et al.* 2008).

- i) The redox potential of electrolyte should be negative as compared to the oxidation potential of the dye.
- ii) The electrolyte should efficiently regenerate the dye after the process of dye excitation and electron injection to conduction band of oxide semiconductor.
- iii) It should have high conductivity
- iv) It should infiltrate the pores of the photoanode and establish contact with both the electrodes.
- v) It should not cause desorption of the dye from the photoanode.
- vi) It should not react with the selant and degrade it leading to poor stability of the cell.
- vii) The absorption of light by the electrolyte in the visible range, in which dye molecules absorb, should be minimum.
- viii) It should not undergo any chemical change leading to loss of its functionality.
- ix) It should be stable up to 80 °C.

Most of the dye sensitized solar cells are based on liquid electrolytes. Efficiencies of 11-12% have been achieved in laboratory scale DSSCs using liquid electrolytes (Yella *et al.* 2011). Short circuit current density and open circuit voltage considerably depend on the electrolyte (Monishka *et al.* 2012; Shi *et al.* 2005). Organic solvent electrolytes were widely used and investigated in dye-sensitized solar cells for their low viscosity, fast ion diffusion, high efficiency, easy to be designed, and high pervasion into nanocrystalline film electrode. The electrolyte used in DSSC mostly contains  $I^-/I_3^-$  redox ions, which mediate electrons between the  $TiO_2$  photoelectrode and the counter electrode. The photocurrent-voltage characteristics are influenced by the nature of cations of the added iodide salts, concentration of iodide and tri-iodide in the electrolyte (Shi *et al.* 2005). The first DSSC used organic liquid electrolyte containing lithium iodide/iodine. Several redox couples like  $Br^-/Br_2$ ,  $SCN^-/(SCN)_2$ , having positive potential as compared to  $I^-/I_3^-$  have been investigated (Hara *et al.* 2001). Organic solvent is a basic component of the liquid electrolytes as it provides an

environment for  $I^-/I_3^-$  dissolution and diffusion. Physical parameters such as donor number, dielectric constant and viscosity affect the efficiency of the cell (Wang *et al.* 2005; Oskam *et al.* 2001).

Bromine ( $Br^-/Br_2$ ) and hydroquinone have also been used as redox electrolyte for DSSC, but the iodine redox electrolyte gives the best performance (Luque *et al.* 2003).  $I_3^-$  is produced at the  $TiO_2$  electrode and consumed at the counter electrode and thus diffused across the electrolyte correspondingly. This is why  $I_3^-$  is often labeled as the hole carrier which draws similarities with the conventional p-n junction solar cells. Similarly,  $I^-$  is produced at the counter electrode and diffused to the opposite direction in the electrolyte (Yanagida *et al.* 2004). Liquid electrolyte based organic solvent usually have high ionic conductivity and excellent interfacial contact property. The redox electrolyte ( $I^-/I_3^-$ ) layer is used for deoxidizing oxidized dye and the platinized carbon nanotubes can collect electrons and catalyze the regeneration reaction of the iodide redox couple. The interaction between carbon nanotubes and electrolyte can actually improve the charge transportation and cell performance. The stability and reproducibility of solid state electrolytes could lead to practical advantages during synthesis and installation compared to liquids (Uddin *et al.* 2013). A report on solid state PEC cells discussed the fabrication of wire-shaped DSSCs using metal wire as working electrode and displayed energy conversion efficiency up to 0.06% (Anandan *et al.* 2007).

### 3.4 Counter Electrode

Like the photoanode and electrolyte, counter electrode is also a vital component of DSSC. In DSSCs, counter electrode act as key factor in receiving electrons from the outer current loop and reducing the  $I_3^-/I^-$  redox mediator. The nature of electron flow is highly correlated with the Counter electrode material type. The purpose of the counter electrode is to complete the electrical circuit of the solar cell and reduce tri-iodide to iodide at the FTO/electrolyte interface and to fulfill this requirement efficiently, the surface of the counter electrode is activated using a suitable catalyst. Low charge transfer resistance is one of the most important characteristics that the catalyst must have. In addition to that, the counter electrode catalyst must also have good chemical stability against electrolyte and high exchange current densities for the reduction of the oxidized form of the charge mediator (Fan *et al.* 2008). Based on these requirements the most commonly used catalyst is Platinum, carbon, conducting polymers etc (Fan *et al.* 2008; Pimanpang *et al.* 2009). The counter electrode serves



to transfer electrons arriving from the external circuit back to the redox electrolyte. It also has to carry the photocurrent over the width of each solar cell. Hence, it must be well conducting and exhibit a low overvoltage for reduction of the redox couple. Till now, Pt has been the desired material for the counter electrode since it is an excellent catalyst for  $I_3^-$  reduction. A Pt thin film deposited on fluorine doped tin oxide substrate typically serves as the counter electrode in conventional DSSCs (Wongcharee *et al.* 2007; Polo *et al.* 2006). Despite the fact that Pt works best among all the catalysts the problem associated with platinum is its excessive cost (Smestad *et al.* 1994). Therefore, optimum usage of platinum is a technological challenge, which, if resolved, can lead to lowering the DSSC cost. An interesting low cost alternative for Pt is carbon, because it combines sufficient conductivity, heat resistance as well as corrosion resistance and electrocatalytic activity for the  $I_3^-$  reduction. Replacing Pt with CNTs was due to several major reasons. Firstly, Pt wires can easily be corroded by electrolytes, which lead to a short life time for cells. The other reason is that the changing of counter electrode materials means different optimization of the interface between carbon based electrodes and coupled electrolyte (Kay *et al.* 1996; Murakami *et al.* 2008). Additionally, the cost of Pt makes it an expensive component. The forms of carbon, which are mostly used for CE application, are carbon black, carbon nanotube and graphene.

#### 4. PHOTO-ELECTROCHEMICAL PARAMETERS

The cell performance will be characterized by several general standards: short-circuit density  $J_{sc}$ , open-circuit voltage ( $V_{oc}$ ), fill factor (FF) and photon-to-current conversion efficiency ( $\eta$ ). The FF is a measure of the junction quality and series resistance of the DSSC and is typically calculated as:

$$FF = \frac{J_m \times V_m}{J_{sc} \times V_{oc}}$$

Where  $J_m$  and  $V_m$  are the maximum current and voltage, respectively. Solar energy-to-electricity conversion efficiency, under sunlight irradiation can be obtained by

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

Where,  $P_{in}$  Power of incident light and measured in  $mWcm^{-2}$  using a solarimeter and  $J_{sc}$  is measured in  $mA cm^{-2}$ .

#### 5. CARBON NANOTUBE ELECTRODE & ELECTROLYTE

It is worth noting that the utilization of carbon materials as counter electrodes has a longer history than other parts of the DSSC assembly. Because of the low cost, high durability, excellent catalytic activity, and electrical conductivity, carbon-based materials have been utilized as effective alternative electrode. The CNTs extraordinary properties such as light weight, excellent mechanical strength, three-dimensional flexibility and outstanding electrocatalytic property, can improve the performance of solar cells (Frackowiak *et al.* 2001; Yakobson *et al.* 2001). CNTs nanostructured surface can also enhance the performance of both charge separation and electron transportation so they can be applied as either a working electrode or counter electrode or even as the conductive substrate (Guo *et al.* 2012). Ramasamy *et al.* (2008), describe the use of spray coated multiwalled carbon nanotubes on FTO glass substrate as counter electrode and the 3d-network of multiwall carbon nanotubes reduced the charge transfer resistance at counter electrode/electrolyte interface and led to an energy conversion efficiency of 7.59 %. Lee *et al.* (2005), showed that the DSSCs light energy conversion efficiency increase with decrease in carbon nanotube counter electrode light transmittance. Dong *et al.* (2011), emphasizes the promise of vertically aligned single walled carbon nanotubes as efficient and stable counter electrode material and the highest conversion efficiency of VASWCNTs- DSSC achieved 5.5 %. Yang *et al.* (2011), explored the aligned CNT sheet as the counter electrode to fabricate dye-sensitized solar cells with high efficiency. A novel working electrode for dye solar cells has been fabricated by Tune *et al.* (2010), it contains incorporation of an array of dye-sensitized single walled carbon nanotubes on ITO glass substrate. Chou *et al.* (2009), fabricate the dye-sensitized solar cells, whose counter-electrode contained a layer of SWCNT/Ag. Most importantly, this study supports the application of SWCNT with the functional group to improve the performance of a DSSC. Li *et al.* (2009), fabricate the porous carbon counter electrodes at low temperature, on F-doped tin oxide conducting glass & achieve efficiency as high as 6.1% compared to that of the cells using sputtering Pt as counter electrode. Imoto *et al.* (2003), prepared a new carbon electrode, he showed that the FF value was particularly improved due to the suppression of back transfer of the photoinjected electrons to the oxidized dyes and or  $I_3^-$  ions. Chang *et al.* (2009), prepared successfully highly efficient photoelectrode of DSSCs using electrophoresis technology. Compared with conventional  $TiO_2$  cell, the  $TiO_2$  -

modified (TiO<sub>2</sub>- CNT) cell achieved an increase in conversion efficiency of 30% & short-circuit current density can be enhanced. Lee *et al.* (2007), fabricated the DSSC using TiO<sub>2</sub>- coated multiwall carbon nanotubes. He showed that the enhancement in short circuit current is attributed to the improved interconnectivity between the TiO<sub>2</sub> particle & TiO<sub>2</sub>- CNTs in the porous TiO<sub>2</sub> film.

DSSC utilizing vertically aligned multi-walled carbon nanotube counter electrode fabricated by Nam *et al.* (2010), and it was found that the vertical alignment realized by low temperature chemical vapor deposition growth of VAMWCNTs directly on FTO glass clearly improved the fill factor thus corresponding cell efficiency as compared to the deposited 2D MWNT films. Hard carbon spherule has been investigated as a counter electrode for DSSCs by Huang *et al.* (2007) and efficiency of the cell reached 5.7% which is comparable to 6.5% of the Pt counter electrode. Single walled carbon nanotubes, Double walled carbon nanotubes and Multiwalled carbon nanotubes have been investigated as electrocatalysts for triiodide reduction in DSSCs by Zhang *et al.* (2011). He concluded that double walled CNTs are found to be a great material for improving charge transport in organic solar cells. Nitrogen doped TiO<sub>2</sub> photoanode, well ordered mesoporous carbon counter electrode was used in DSSC studies by Miao *et al.* (2011). He achieved the efficiency of 10.10 % compared with undoped - DSSC efficiency of 8.90 %. DSSC based on ZnO/MWCNT nano composite films are prepared by Ramar *et al.* (2012) and the photoelectric performances of this DSSC with various concentrations are compared. Battumur *et al.* (2012), found that the photovoltaic performance was strongly influenced by the concentration of graphene nanosheet in composite electrode. Multiwalled CNT./ Lee *et al.* (2008), fabricated the DSSC with the photoanode using CIGS/CdS/SWNTs /FTO as the anode and the super-strate type CIGS cells show high power conversion efficiency, due to the addition of the SWCNTs layers in the photovoltaic cell. The SWCNTs layers in the photovoltaic cells allow for the formation of an efficient electronic energy cascade structure and decrease the interfacial resistance, as well as improving the electrical field. DSSC incorporated with TiO<sub>2</sub> porous films prepared at a low temperature along with MWCNT containing 2 different electrolytes were investigated by Lee *et al.* (2008) with 0.1 wt% MWCNT/ TiO<sub>2</sub>, the DSSC had the highest cell performance and the longest electron lifetime in the TiO<sub>2</sub> electrode (Ting *et al.* 2010). Recently Swati *et al.* (2012), used carbon nanotube as a counter electrode in DSSC and obtained the maximum efficiency of 3.7%.

Incorporation of carbon nanotubes into polymer solar cells is of interest because unique morphological properties of carbon nanotubes such as high surface area and extremely low percolation threshold can facilitate efficient exaction dissociation and fast charge carrier transport. The effect of incorporating different types of carbon nanotubes such as Single -walled, Double walled and Multiwall carbon nanotubes in organic solar cells was studied by Andres *et al.* (2008). The addition of CNT to the polymer increases the power conversion efficiency by 3 orders of magnitude compared with device without CNTs. Li *et al.* (2007), demonstrates the fabrication of low cost polymer: C<sub>60</sub> -SWNT composite & achieved the efficiency of 0.57 %. He showed the introduction of SWCNT in to the composite not only enhances the short circuit current density, but also improves power conversion efficiency as compared to cells without SWCNTs. The influence of adding functionalized Multiwalled carbon nanotubes to the PEDOT: PSS buffer layer on the performance of polymer solar cells has been studied by Lee *et al.* (2010), It improves the optical transmittance and short circuit current density. Miller *et al.* (2006) demonstrated that multiwalled carbon nanotubes have strong potential as an interpenetrating, hole extracting electrode in organic solar cells & improve the power conversion efficiency to 0.46% compared to reference.

The first doping reactions by K and Rb were performed on multiwall carbon nanotubes prepared by electrical discharge method (Zhou *et al.* 1994). Multiwalled carbon nanotubes can also be doped with light alkali metal such as Li. A lot of work has been focused on Li electrochemical doping of MWCNTs, because of the interest in Li-ion batteries anode application (Maurinet *et al.* 1999). Suzuki *et al.* (1998), proved that the SWCNTs can be reversibly intercalated with Cs or K. Jin *et al.* (2000), showed that the Multiwall carbon nanotubes have been doped with electron acceptors like F<sub>2</sub>, Br<sub>2</sub>, Cl<sub>2</sub>. MWNTs have been intercalated with larger molecules such as metallic chloride. Bower *et al.* (1998), doped SWCNTs with nitric acid a charge transfer spontaneous reaction can arise.

According to Sumanasekara *et al.* (1999), the spontaneous electrochemical doping of SWNTs by Sulphuric acid yields to the intercalation of H<sub>2</sub>SO<sub>4</sub> and HSO<sub>4</sub><sup>-</sup> molecules in the interstitial channels within the bundles between the tubes. Lee *et al.*, reported that the bromine doped SWNT bundles show a remarkable enhancement of conductivity and a typical metallic character in temperature dependence.

**Table 1. Photoelectrochemical Parameters of Carbon Nanotube Based DSSCs**

S.N o.	Working electrode	Counter electrode	Dye	Electrolyte	V <sub>oc</sub> (V)	j <sub>sc</sub> (mA cm <sup>-2</sup> )	FF	η(%)	References
1.	TiO <sub>2</sub> on FTO	Multiwalled CNT on FTO	N719	0.5M 1-butyl-3-methylimidazolium iodide, 0.05M iodine, 0.1M guanidine thiocyanate & 0.5M 4-tert-butyl pyridine	0.783	5.64	.62	.59	Ramasamy et al. 2008
2.	TiO <sub>2</sub> on FTO	CNT on FTO	Red dye	I <sup>-</sup> /I <sub>3</sub> <sup>-</sup>	0.690	1.5	9	.88	Lee et al. 2005
3.	TiO <sub>2</sub> on FTO	Vertically aligned single walled carbon nanotube	N719	50 mM I <sub>2</sub> , 500 mM LiI, 500 mM 4-tert-butyl pyridine & 2-methoxy propionitrile	0.65	13.8	61	5.5	Dong et al. 2011
4.	TiO <sub>2</sub> on FTO	CNT sheets on FTO	N719	Li I, I <sub>2</sub> , 1,2 -dimethyl -3-propylimidazolium iodide & tri-butyl-phosphate				6.6	Yang et al. 2011
5.	Pt on FTO	Single walled CNT on ITO	N3 ruthenium dye [cis-bis (4,4'-dicarboxy - 2,2'-bipyridine) dithiocyanato ruthenium (II)]	3-methoxy propionitrile containing 1-propyl 3-methylimidazolium iodide, iodine and benzimidazole )	0.043	0.002	0.28		Daniel et al. 2010
6.	TiO <sub>2</sub> on FTO	Single walled Carbon nanotube on FTO	N719	20 ml of propylene carbonate , 0.254g of iodine & 1.66g KI					Chou et al. 2009
7.	TiO <sub>2</sub> on FTO	Carbon counter electrode on FTO	N3	0.6 M PMII, 0.05 M iodine, 0.1 M L I & 0.5 M tert-butyl pyridine in 3-methoxypropionitrile	0.618	0.0145	67.5	6.1	Li et al. 2009
8.	TiO <sub>2</sub> on FTO	Carbon counter electrode on FTO	N3	0.1M LiI, 0.3 m 1,2-dimethyl -3 -propyl-imidazolium iodide, 0.05M iodine & 0.5 M tert-butyl pyridine	0.808	7.93	60.7	3.89	Imoto et al. 2003
9.	TiO <sub>2</sub> on FTO	TiO <sub>2</sub> - CNT film	Natural dye extracted from ipomoea	I <sup>-</sup> /I <sub>3</sub> <sup>-</sup>	0.56	1.14	0.56	0.359	Chang et al. 2009
10.	TiO <sub>2</sub> - CNT	Pt	0.3mM [RuL <sub>2</sub> (NCS) <sub>2</sub> .2H <sub>2</sub> O]	0.8M LiI, 40mM Iodine & 0.2 M 4-tert-butyl pyridine	0.63	13.5	0.59	4.97	Lee et al. 2007

Table 1. cont....

11.	TiO <sub>2</sub> on FTO	CNT counter electrode	N719	0.6 M butyl methylimidazolium iodide, 0.03 m I <sub>2</sub> , 0.1M guanidiniumthiocyanate and 0.5 M 4-tert-butyl pyridine	0.0738	15.27	0.69	8.03	Nam et al. 2010
12.	TiO <sub>2</sub> on FTO	Carbon counter electrode on FTO		0.6M dimethylpropylimidazoliumiodide, 0.1 M iodine, 0.5M tert-butyl pyridine, 0.1m LiI				5.7	Huang et al. 2007
13.	TiO <sub>2</sub> on FTO	Double walled CNTs	N719	0.1M Guanidine thiocyanate 0.03M iodine, 1 M 1-methyl-3-propylimidazolium iodide & 0.5 M tert-butyl pyridine	0.8	15.43	0.652	8.03	Zhang et al. 2011
		Single walled CNTs			0.8	14.94	0.640	7.61	
		Multiwalled CNTs			0.8	15.25	0.564	7.06	
14.	N-doped TiO <sub>2</sub>	Well orderedmesoporous carbon	N719	0.03M iodine, 0.06 M LiI, 0.6M 1-butyl - 3-methylimidazolium iodide, 0.1M guanidiniumthiocyanate& 0.5 m 4-tert-butyl pyridine				7.5	Miao et al. 2011
15.	Zno/MultiwalledCNTcomposite	Pt	N719	0.3M 4-tert-butylpyridine, 0.5M LiI,0.05M iodine				2.77	Ramar et al. 2012
16.	TiO <sub>2</sub> on FTO	Multiwalled CNTs/GNS composite	N719	0.6M dimethyl-propylimidazolium iodide, 0.1M iodine, 0.5M tert-butyl pyridine, 0.1M LiI	0.81	6.4	0.57	3	Battumur et al. 2012
17.	Multiwalled CNTs with TiO <sub>2</sub>	Pt on FTO	N3	0.MLiI , 0.05m iodine, 0.5M TBP	0.781	9.08	0.708	5	Lee et al. 2008
18.	TiO <sub>2</sub> on ITO carbon black as a bridge	TiO <sub>2</sub>	Alizarin yellow	0.05M iodine, 0.5M KI				2.5	Ting et al. 2010
19.	TiO <sub>2</sub> on FTO	Carbon nanotube	Ruthenium polypyridine	I <sup>-</sup> /I <sub>3</sub> <sup>-</sup>	0.653	0.00376	49	3.7	Swati et al. 2012



Kyaw *et al.* (2012), utilized p-doped CNT as a working electrode by the treatment of SWNT with sulfuric acid. The acid treatment generates defects (COOH and SO<sub>3</sub>H functionalities) on CNT and the produced chemical functionalities are beneficial for enhancing the electrical conductivity in the CNT film. The sulphuric acid p-dopes the CNT by oxidation and the attachment of chemical functionalities helps us to stabilize p-doping owing to their electron-deficient property. Aliaga *et al.* (2008), found that the functionalization of individual SWNTs by electro deposition of Prussian blue, (Fe<sup>III</sup> [Fe<sup>II</sup> (CN)<sub>6</sub>]<sub>3</sub>. nH<sub>2</sub>O) leaves metallic tubes unaffected, whereas semiconducting tubes are strongly p-doped. The temperature-dependent electrical properties of Prussian blue – functionalized semiconducting tubes can be understood by the freeze-out of the transfer of holes from the PB to the nanotube below 100K.

Tantang *et al.* (2012) demonstrated that DSSCs with bilayer CNT-based transparent counter electrode (combining highly conductive normal CNTs and highly electrocatalytic N-doped CNTs) showed a significant improvement compared to DSSCs with normal CNT counter electrodes and achieved a maximum power conversion efficiency of 2.18%. Lee *et al.* (2011), presents the remarkable device performance enhancement in Bulk heterojunction solar cells employing N or B- doped CNTs as highly selective electron or hole –transport enhancement materials. The highest efficiency of B-CNT & N-CNT solar cells was found to be 4.1% and 3.7% respectively. N- CNT may play the role of a bridge, helping the electron transfer. Incorporation of B-CNT in Poly 3-hexyl thiophene can enhance the hole transport. He confirmed that doped CNTs in the BHJ active layer are highly desirable for solar cell performance. Ramuz *et al.* (2012), utilized n-type doped carbon nanotubes was used as a cathode in all carbon solar cells.

The development of a gel polymer electrolyte for high performance and high stability DSC is of critical importance and high priority in terms of accelerating the commercialization process of DSC. It is well known that the performance of a DSC is strongly dependent on the transport property of the electrolyte. A hybrid of polymer-dispersed multi-walled carbon nanotubes was utilized in networking with the conventional composition of gel electrolyte in dye-sensitized solar cells to purposely enhance the cell efficiency (Wang *et al.* 2012). Khongchareon *et al.* (2013) achieved the maximum efficiency of 0.75% with 5 wt% of the MWCNTs in the polyethylene glycol gel polymer electrolyte.

## 6. CONCLUSION

In summation, replacing key components of dye sensitized solar cells with carbon nanotubes will make them cheaper, easier to produce, longer lasting and more flexible than they currently are. Current rate of fossil fuel usage will lead to an energy crisis this century. All Carbon based solar cells have the possibility to revolutionize the movement for different, more efficient, and green energy in near future. Although the efficiencies obtained with the carbon nanotubes electrode are below the requirements for large scale production, the results are hopeful and can boost additional studies oriented to the search of new carbon based solar cell and to the optimization of solar cell components compatible with such electrodes. All Carbon nanotube gives a novel route to green technology.

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